Methyl Chloride via Oxyhydrochlorination of Methane: A Building Block for Chemicals and Fuels from Natural Gas

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Abstract

The objectives of this cooperative agreement are to develop the oxyhydrochlorination (OHC) process for the conversion of methane to methyl chloride. In the first Phase of the project, Dow Corning has developed a stable selective catalyst and demonstrated the technology on a laboratory and a pilot plant scale. The current effort builds on earlier learning to pilot the technology on an engineering scale, integrated operation, and to obtain design, scale-up, and cost data for a commercial-scale process economic evaluation.

Significant progress has been completed in Task 1 with the objective to complete a fundamental technical and economic evaluation of learning gathered the Phase I effort of this project. A decision to proceed with the project will be made after completion of this Task.

A computer model of the reactor system has been developed, which includes heat and mass transfer effects as well as reactions. Model validation is in progress.

The Absorber/Stripper technology evaluated and implemented on the Phase I PDU to recover chlorocarbons (including methyl chloride) from reaction products has been scaled to evaluate economics for a commercial scale plant. In a parallel exercise, alternate recovery technologies were investigated for economic evaluation, to assure that the minimum capital option is pursued for the Phase II design.

Commercial scale plant equipment and total plant costs are being evaluated using information from the Phase I PDU, reactor modeling and recovery system evaluation to estimate capital and operating costs for a commercial scale OHC unit.

Table of Contents

List of Graphical Materials

List of Tables

Executive Summary

Dow Corning has been conducting research on methods for producing methyl chloride from methane under a cooperative agreement with the U.S. Department of Energy, the Gas Research Institute and the Texas Gas Transmission Company. In Phase I of this effort, Dow Corning developed a stable selective heterogeneous catalyst and demonstrated the technology on a laboratory and pilot scale. However, significant technical challenges, including materials of construction, product recovery, reactor performance and reactor temperature control were encountered.

Phase II of the effort is also supported by a cooperative agreement with the US DoE and with GRI. Following a critical evaluation of the new technology, an integrated engineering-scale pilot facility will be constructed and operated to build on the current development and gather sufficient engineering information to design and build a commercial scale plant.

Phase II has begun with a thorough evaluation of the Phase I technology development to date--including the current understanding of technical risks, feasibility and economics--to make a go/no-go decision to proceed with Phase II.

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Introduction

Dow Corning has been conducting research on alternate methods for producing methyl chloride since 1982. Methyl chloride (CH_3Cl, or MeCl) is used as an intermediate material in silicones production and Dow Corning is the world's largest producer of both. Current technology involves reaction of methanol (CH_3OH, or MeOH) with HCl to produce CH_3Cl and water:

$$CH_3OH + HCl \text{ ----> } CH_3Cl + H_2O$$

Because of methanol's market price volatility, lower cost and more price-stable starting materials are sought for Dow Corning's silicones production. Oxyhydrochlorination (OHC) utilizes methane in a gas phase heterogeneously catalyzed reaction with HCl and oxygen to produce methyl chloride and water:

$$CH_4 + HCl + {}^1/_2\, O_2 \text{ ----> } CH_3Cl + H_2O$$

Similar side reactions occur to convert the CH_3Cl product to methylene chloride (CH_2Cl_2), methylene chloride to chloroform ($CHCl_3$) and chloroform to carbon tetrachloride (CCl_4), but these reactions occur to a much lesser extent than the one shown. Another family of side reactions is combustion of these chlorocarbon products to form CO or CO_2, H_2O and HCl. Suppression of all of these reactions is desirable to maximize yield of methyl chloride. The combustion reactions are more prevalent at elevated temperatures making reactor temperature control particularly important.

Specific tasks to achieve Phase II objectives have been developed as follows:

TASK 1	Fundamental Technical and Economic Evaluation
TASK 2	Catalyst Selection Optimization and Characterization Studies
TASK 3	Pilot Plant Design
TASK 4	Pilot Plant Detailed Engineering, Procurement and Construction
TASK 5	Pilot Plant Startup and Operation
TASK 6	Pilot Plant Process Optimization
TASK 7	Pilot Plant Extended Operation
TASK 8	Pilot Plant Economic Evaluation/Scale-up Decision

Efforts have begun in TASK 1.

Results and Discussion

Significant progress has been achieved in Task 1 with the objective to complete a fundamental technical and economic evaluation of all information and learning gathered in the design, operation and troubleshooting of the oxyhydrochlorination pilot unit in Phase I. A decision to proceed with the project will be made after completion of this Task.

Subtask 1.1 Reactor

A spreadsheet computer model of the reactor system has been developed, which includes heat and mass transfer effects as well as reactions. Energy balances are conducted for the catalyst particles and for the bulk fluid phase. Heat generation, conduction and transfer out of the reactor is considered. Chlorination reactions and methyl chloride combustion reactions are included and kinetic effects are included. This work currently requires assumptions of the intrinsic kinetic information which will be subsequently developed in Task 2, but the kinetics are being approximated using laboratory and pilot plant data generated in Phase I. Unfortunately, the data is confounded by poor reactor temperature control, so it is not possible to accurately determine the intrinsic kinetics with this data. However, an example of model output and pilot plant results for a single experimental run is given below to illustrate the potential for the approach.

Table 1: Example Model and Pilot Plant Results

	Model results vs. Pilot Plant Results		
	Actual	Model	% error
HCl Conversion	62.4%	62.4%	0.0%
CH4 Conversion	13.8%	14.6%	5.6%
CH3Cl Selectivity	64.0%	65.0%	1.4%
CH2Cl2 Selectivity	14.3%	14.4%	0.3%
CO2 Selectivity	18.5%	17.8%	-3.3%

The model will be used to match data gathered in the PDU to model the temperature profiles and reactor performance observed. The model will allow exploration of reactor conditions which will minimize temperature excursions and temperature gradients which adversely affect performance, and examination of parameters which can improve performance.

Subtask 1.2 Recovery System

The recovery system for the oxyhydrochlorination reactor product must separate chlorocarbon products (chiefly MeCl) from unreacted methane and HCl, CO_2 byproducts and generated water. Methane is recycled to the reactor (CO_2 byproducts are removed as a purge stream), the HCl and water are a waste stream and the chlorocarbons are separated by distillation. The final distillation of chlorocarbons is very straightforward and not subjected to detailed alternatives investigation, but the reactor product recovery was evaluated.

The Absorber/Stripper technology evaluated and implemented on the Phase I has been scaled to develop economics for a commercial scale plant. In a parallel exercise, alternate technologies are being developed and sized for economic analysis also, to assure that the minimum capital option is pursued in the Phase II design. Materials of construction were considered in this evaluation to minimize costs without introducing undue safety, environmental or operational risks. Recovery system alternatives included direct contact condensation of the reactor products using recycled chlorocarbons (with and without a pre-condenser), distillation, and several options for removing unreacted HCl prior to all other separation steps to eliminate the downstream requirement for corrosion-resistant materials of construction, as well as pressure-swing-absorbtion (PSA).

Direct contact condensation and distillation options for removing chlorocarbons from the reactor product were determined to be impractical due to the high required flow rate of recycled chlorocarbons for condensation duty, the large size of heat exchangers needed, and the high equilibrium MeCl concentrations remaining in non-condensed streams. PSA was not pursued due to high costs associated with large equipment size. These evaluations confirm the choice of the absorber/stripper technology made in Phase I. However, removal of HCl from the reactor product stream was shown to be a useful approach to relax construction materials requirements--and associated equipment costs.

Subtask 1.3 Economic Evaluation

Commercial scale plant equipment and total plant costs are being evaluated using information from the Phase I PDU, reactor modeling and recovery system evaluation to estimate capital and operating costs for a commercial scale OHC unit. These costs have been compared with savings realized by utilizing methane in place of methanol as a feedstock to determine if the OHC technology is viable based on projected prices for methane and for methanol. The raw material savings is based on the cost of one mole of methanol versus one mole of methane and one half mole of oxygen (refer to the OHC reaction in the Introduction). In addition, the conventional technology uses a small amount of H_2SO_4 to scrub an impurity from the MeCl product, while OHC does not and this generates a small additional savings.

Historical costs of methanol and methane provide an indication of the magnitude of benefits. As an example, for methanol at \$0.12/liter (\$0.45/gallon), methane at \$108/1000 m^3 (\$3.05/1000 ft^3) and oxygen at \$38.8/1000 m^3 (\$1.10/1000 ft^3) the following savings would be realized:

Conventional Technology		OHC Technology	
		Methane:	\$1.026/mole
Methanol:	\$2.093/mole	Oxygen:	\$0.197/½ mole
TOTAL:	\$2.093/mole MeCl		\$1.223/mole MeCl

Difference: \$0.870/mole MeCl or \$0.037/kg (\$0.017/lb) MeCl

Additional operational savings are realized by elimination of the H_2SO_4 scrubbing step and additional costs are associated with methane purity requirements, so this difference is adjusted (upward) slightly.

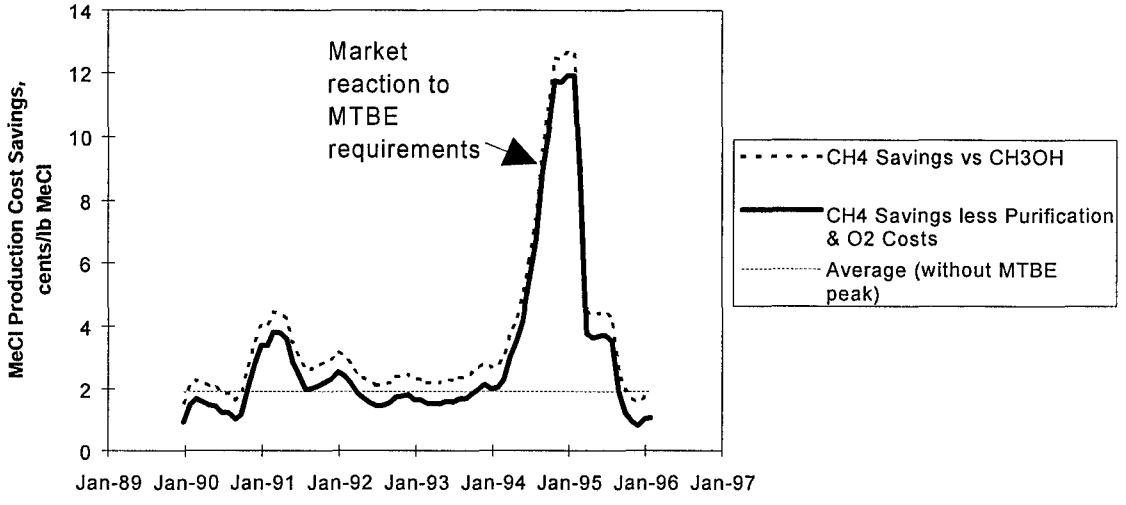
Assumptions: HCl feeds are not accounted for in this example; it is assumed that the OHC technology will be optimized to be similarly efficient in HCl consumption as the conventional process.

The above analyses also assume that unconverted methane (most will be recycled) will be consumed locally as fuel and does not incur a cost penalty to the economics.

Also, byproducts of methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$) and carbon tetrachloride (CCl_4) are assumed to be sold for further processing by others on an at-cost basis. Dow Corning has identified a potential customer for these materials.

The calculation is repeated using historical methanol and methane prices over the last five years to illustrate the likely magnitude of the savings, as shown in the figure below:

MeCl Production Cost Savings Based on Historical Price
DIFFERENCE Between MeOH and CH4

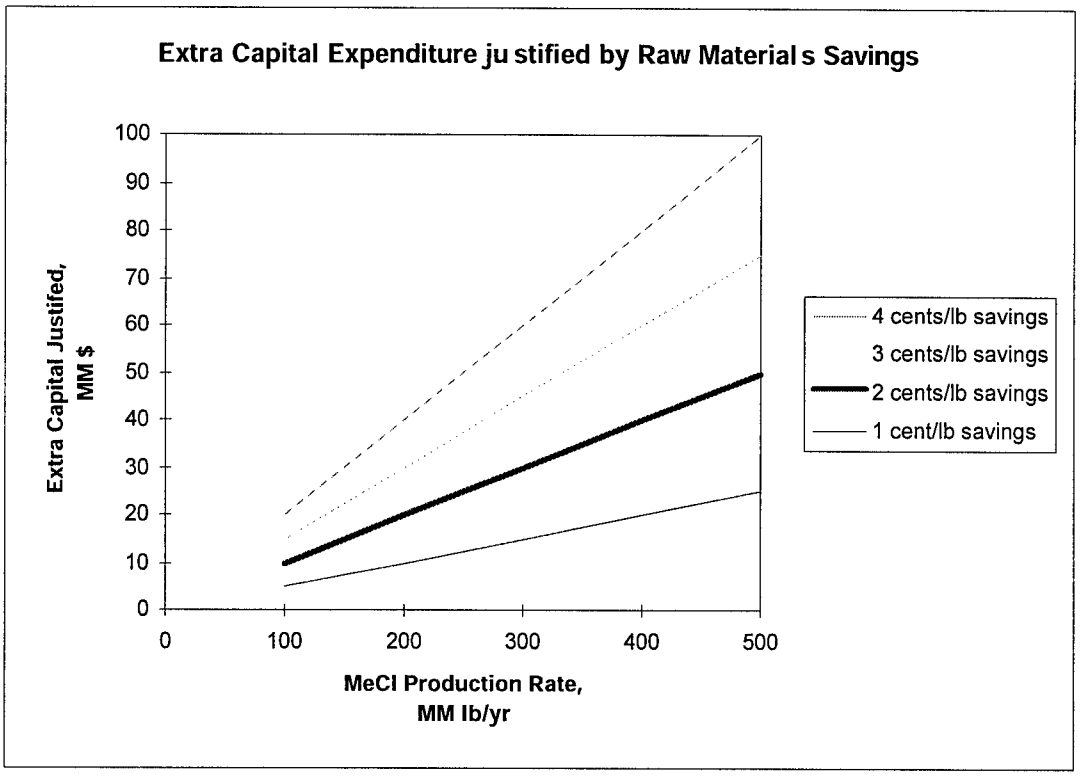


Data sources: CH_3OH - Chemical Marketing Reporter
CH_4 - Energy Information Administration, Natural Gas Monthly
O_2, CH_4 purification and H_2SO_4 - commercial quotations

The sharp peak in the difference is a result of US Clean Air Act Amendments requiring re-formulated gasoline in certain designated areas. This caused the methanol market to react due to increased demand on methyl tert-butyl ether, a gasoline additive produced from methanol. However, producers added excess capacity and the federal government allowed some states to opt out of using reformulated gasoline; the market plummeted. If this peak is ignored, the average savings for methyl chloride using methane instead of methanol is about 4 cents/kg (2 cents/lb).

Dow Corning recognizes that the OHC technology will be more expensive to design and build than conventional technology for producing methyl chloride using methanol feedstock, owing to process complexity, lower per-pass conversions and challenging materials-of-construction issues. However, the savings highlighted above allow additional capital investment while still achieving an economically advantageous plant.

A simple analysis considers payback of the raw material savings provided by OHC. This savings pays back the extra capital spent in excess of conventional technology. If a five year payback criteria is used--that is: additional capital invested is returned by the savings of five years' operation--the following chart illustrates the additional capital which can be invested on OHC at various savings rates for MeCl production:



So, conservatively, at 4 cents/kg (2 cents/lb) savings for MeCl for a 227 M te/yr (500 MM lb/yr) methyl chloride production rate, an OHC plant can be economically justified at $ 50 MM additional capital ABOVE capital costs for the conventional technology.

Dow Corning is currently evaluating the capital costs for the OHC technology, bearing in mind the technical hurdles Phase I work has identified. The major issues are materials of construction challenges, recovery and separation of products and reactor performance and heat transfer.

Any practical alternatives which are identified during the technical and economic evaluation which could increase the chance for a successful technology commercialization without imposing undue risk or uncertainty will be considered for replacing the existing technology definition. The DoE Project Officer will review and approve any such changes in use of DoE funds.

A decision to proceed with Phase II of the project will be made when these factors are developed and considered by Q2 1997.

Data Reduction, Interpretation, and Analysis

No experimental data was generated in this Quarter of the Phase II effort.

Conclusions

The oxyhydrochlorination reactor can be modeled, but intrinsic kinetic information is needed to realize the full power of this technique. However, it appears that some learning of important reactor parameters needed to optimize performance will be developed in advance of rigorous evaluation of the reaction mechanism.

Recovery system alternative evaluations have confirmed that the absorber/stripper separation technique developed in Phase I is the appropriate choice for removing chlorocarbons from the reactor product, and can be improved by removal of HCl from the reactor product to allow use of less robust--and less costly--construction materials.

Simple economic evaluation confirms that about $ 50 MM extra capital can be spent on a 227 M te/yr (500 MM lb/yr) MeCl production rate OHC plant and still achieve acceptable payback through raw material savings in comparison with methanol-based technology. Capital cost estimation on the best achievable design and reactor performance continues to determine if the oxyhydrochlorination technology can be executed within these constraints.

List of Acronyms and Abbreviations

DoE	U.S. Department of Energy (Pittsburgh Energy Technology Center)
FTIR	Fourier Transform Infrared (analyzer used to quantify reaction products)
GRI	Gas Research Institute
hr	hour
kg	kilogram
lb	pound
M	thousand (1,000)
MM	million (1,000,000)
MeCl	Methyl Chloride, chloromethane, CH_3Cl
MeOH	Methanol, CH_3OH
MTG	Methanol to Gasoline (process)
OHC	Oxyhydrochlorination
PDU	Process Development Unit -- Phase I pilot plant
PSA	Pressure Swing Absorbtion
Phase I	Catalyst development, laboratory and pilot plant demonstration of feasibility of oxyhydrochlorination to produce methyl chloride from methane.
Phase II	Technical evaluation, catalyst development, engineering scale demonstration and optimization for commercial scale-up of oxyhydrochlorination to produce methyl chloride from methane.
te	tonne, metric ton (1,000 kg)
yr	year